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CONTRACTOR: UNIVERSITY OF GUELPH

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R E P O R T
on
CANMET CONTRACT

(Serial 23440 - 7 - 9001/01-ST)
Due Date: October 31, 1987

1. PIXE Spectrum Fits

All spectra supplied have been processed and the results submitted to Dr. L. J. Cabri.

2. Auxiliary Computing

All auxiliary calculations (matrix integrals, detection limits, etc.) have been submitted to Dr. L. J. Cabri.

3. Quality of Spectral Fits

The choice of absorber thickness in these spectra was unfortunate. It resulted in very intense matrix x-ray peaks (Fe, Cu, etc.) compared to trace element peaks. These former peaks have strong low-energy tailing. Presently, our code does not include a tail model (and if it did, it would not be appropriate for the Heidelberg detector). The fit optimization is dominated by these strong, tailed peaks and the result is a distortion of the energy calibration. This is so severe that in a pyrrhotite standard, the Pd peak is so distant from the calibration prediction that Pd is rejected as a constituent.

Our solution to this was the obvious one of doing separate fits to the matrix x-ray region and to the higher-energy trace element regions. This worked perfectly well for peak intensities. However, this separation prevented us from using our standard recipe for error calculation; this involves comparing the fitting code's stated error on a matrix peak intensity with the true square root error from counting statistics, and correcting all other errors by that ratio. We therefore devised a new approximation for error estimation, based on combining in quadrature the square root counting error in each peak area with the corresponding error in the fitted background. While this recipe is rigorous only for an isolated peak on a smooth background, it is a reasonable estimate for more practical situations.

4. Detection Limits

In future exercises, a set of synthetic minerals free of trace elements should be run to ascertain the ultimate detection limits.

5. Auxiliary Details

See Attached Material.

7pp

MICROMEDIA

REPORT ON CANMET 87 PIXE FITS

1. STANDARDS and DETECTOR/FILTER DATA

FeS(SePd) with 200 Al: Separate Fits to the (SePd) and Fe regions (B)

Run	Se	Pd	Fe
RGC 14	5092	1919	301228
RGC 16	4318	1825	289561
S641-2	4555	1825	301493
S641-4	6870	2077	301826
-6	6340	1775	303282
-7	7144	1857	306478
-8	7295	1842	304492
Mean	5945	1891	for 1.5 Ruth

with 350 Al:

Run	Se	Pd	
S641-5	3027	1671	for 1.5 Ruth

FeS(CuPd) with 200 Al - Separate Fits to (CuPd) and Fe region (B):

Run	Cu	Pd	Fe
S646-1*	3928	4026	387776
5	2890	3340	298378
6	3040	3786	311549
7	2966	3816	310054
8	2857	2762	298298
Mean of 4	2938	3426	for 1.5 Ruth

* excluded because Fe count was anomalously high.

Copper(AgAu) with 350 Al

(Runs with 200 μm AL and Be are not usable)

Run	Au	Ag	Ruth
659-1	503	2991	2.5
2	669	2802	2.5
4	568	3338	2.5
5	842	3803	3.5
6	627	4176	3.5
Mean	335	1780	for 1.5 R

Standard 661 is below the detection limit for Au and uncomfortably near it for Ag.

Detector/Filter Data

Z		ξ_Z^I	$T_\gamma(200)$	$T_\gamma(350)$
24	Cr	.968	2.214×10^{-4}	0
26	Fe Kα	.977	.00609	.000133
27	Co	.979	.0176	.000850
28	Ni	.980	.0396	.00352
29	Cu	.981	.0743	.0106
30	Zn	.981	.1214	.0250
31	Ga	.980	.1791	.0493
33	As	.976	.3100	.1288
34	Se	.972	.377	.182
40	Zr	.935	.700	.535
41	Nb	.924	.736	.585
44	Ru	.871	.821	.707
45	Rh	.846	.842	.740
46	Pd	.816	.861	.769
47	Ag	.784	.877	.795

Standards

FeS(SePd) $I(Se) = 1.201 \times 10^6$ per μ C per s.
$I(Pd) = 0.178 \times 10^6$ per μ C per s.

With 200 μm Al:

7 runs → Mean Se count = 5945 for 1.5×10^5 Ruth
Mean Pd count = 1891

Use Yield = H Cz I ξ $e^{-\mu x}$
Put Cz = 0.9 for Se
∴ H = 0.0150 Mean
Put Cz = 1.1 for Pd → H = 0.0137 .0143

With 350 μm Al:

1 run → Se = 3027, Pd = 1671
∴ For Se, H = 0.0158
For Pd 0.0136

FeS(CuPd) $I(Cu) = 1.812 \times 10^6$
$I(Pd) = 1.780 \times 10^6$

With 200 μm Al, 4 runs give: Mean Cu = 2938 (Cz = 1.8)
Mean Pd = 3426 (Cz = 1.6)

∴ H(Cu) = .0124
H(Pd) = .0171 Mean .0147 agrees well

Cu(AgAu) I(Ag) = 1.422×10^5
I(Au) = 2.522×10^5 (CC with $L\alpha/Lx = .568$)

5 runs with 350 μm Al normalized to 1.5 Rutherford

Mean Au $L\alpha$ = 335, mean Ag $K\alpha$ = 1780
Concs Cz = 1.55

. . H(Ag) = 0.0130
H(Au) = 0.0119 Mean 0.0125

2. COMMENTS ON SPECIMENS

Pyrrhotites: Lower region fitted with FeNi showed residue at ~6.9 keV, but inclusion of Co in fit had no effect and gave no significant Co intensity. Hence residue is due to Ni tailing, and final fits excluded Co.

Chalcopyrites: Poor χ^2_7 in FeCu region reflects strong peak asymmetry, very visible at high intensities. Filter was wrongly stated in Canmet notes for LCP2: it is 200 μm.

Pyrites: Better fits with FeCo than with FeCoNi. Conclude Ni absent.

Pentlandites: Addition of Co improves fits, so Co is present. Note severe pileup of FeCoNi in 13-17 keV; this prevents us looking in that region.

Copper anodes: No gold seen, but silver seen in most cases. Do not use H value but simply scale from 1.55% concentration via the peak areas in specimen and standard.

3. DETECTION LIMITS

See computer print-outs for some representative spectra.

4. MATRIX INTEGRALS

See computer printouts.

5. PEAK AREAS

See written sheets.

SUMMARY OF STEPS TAKEN FOR CABRI/87 DATA FITS

Due to the possible non-linearity of the Heidelberg system in terms of channel number versus energy, and to the problems associated with the highly assymetric matrix peaks (our code does not yet incorporate a tailing correction) several extra steps had to be taken in the processing of these data in order to acheive the most accurate measurement of both the peak areas and their associated errors.

The possible problem of non-linearity can be easily seen in a standard spectrum such as one containing FeSePd. When the fit is done over the entire region, the routine moves the energy calibration parameters so as to miss the Pd peak altogether as this is the least influential peak of the three in terms of intensity. In other words the stronger Fe ans Se peaks set a calibration that is incompatible with the Pd. Another explanation for this problem may be that the large tails on the matrix peaks (Fe in this case) may cause the routine to adjust the energy parameters to erroneous values.

Energy Calibration: Channel # = A1+A2*E

The large tails also pose another problem. In order to achieve the best possible fit, the width parameters are both allowed to vary in the fitting procedure. Two problems then arise. The fact that both parameters are varying contributes to an overstatement of the error due to the strong correlation between them. The second problem comes in when a wide region of fit is taken and the heavily tailed matrix peaks then have the dominant role in determining A3 and A4, which will emerge as larger than they should be.

Width Calibration: Width = A3+A4*E

SOLUTIONS

In what we might call round one of fitting, through the fitting of standards we were able to see the problems of trying to vary the energy dependent width parameter as well as the problem of fitting too large a spectral region. A second round was therefore done in which the suspected elements (as determined from the plots) were included in fits to smaller segments of the spectra rather than the entire spectra being used. These were then tabulated and conclusions drawn as to which elements were actually present and whether their errors were of a sensible nature. One example is the case of pyrrhotites where Co was initially included; in the second round it was excluded and consideration of the two sets of data led us to conclude that the apparent Co peak arose from the presence of nickel; hence Co was not included in the final data set reported.

From these results, it was realized that even with the smaller sized - regions of fit, A4 had to be fixed in order to get reasonably sensible error estimates. The latter were then refined via the assumption that the matrix peak should have an error of about one sigma. From this, all other errors on areas were normalized by the factor by which the computed matrix error deviated from its square root statistical error . These various modifications were all included in a final all-encompassing round, the results from which are tabulated.

MDL VALUES

Contrary to the method used in the past, where rough integration of the spectral background corresponding to the peak of interest was done, a program has been written that uses the known calibration parameters for linewidth and energy to compute the MDL value for that element in the particular spectrum. A valid test of its soundness is the observation of very high MDL values where the matrix peaks occur. MDL values are given for all Z values between 11 and 52 so that this check may be done.